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Geometry and electronic properties of Cu_n ($n \leq 9$)*

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The equilibrium geometries and the atomization energies of Cu_n ($n \leq 9$) clusters have been calculated using the B3LYP/LANL2DZ method. It is shown that the clusters do not copy the bulk structures and undergo significant geometrical changes with size and the atomization energy per atom increases monotonically with size. By analysing the energy level distribution, the Fermi level, HOMO–LUMO gaps, the electron affinities and the ionization potentials are calculated and the results are in reasonable agreement with experiment. These electronic properties are found to be strongly structure dependent, which can be used to determine which of the low-lying structures is observed experimentally.

Keywords: copper clusters, equilibrium geometries, atomization energy, electron affinity, ionization potential

PACC: 3640, 3640B, 3120A, 3130J

1. Introduction

The geometric and electronic structures of small metal clusters of the group 1B are currently of considerable interest, and in particular, copper clusters have attracted much attention. Because of the peculiar nature of the electronic structure ($3d^{10}4s^1$) of the Cu atom with one s electron outside a closed d shell, Cu clusters are expected to have some similarities with alkali metal clusters. Meanwhile, the small energy difference between the atomic s and d levels suggests that hybridization effects may play an important role at small cluster sizes in determining the electronic and structural properties of Cu_n clusters.

In order to determine the electronic structure of metal clusters in detail, a number of experimental and theoretical studies have been made. The ultraviolet photoelectron spectra of mass-selected negative copper clusters have been measured to probe the 4s valence band structure.[1] Optical spectroscopy of matrix-isolated Cu atoms and small Cu clusters yields information about the electronic level structure.[2] The photoelectron spectra of Cu_n^- (n=1–10) are presented for electron binding energies up to 3.35eV at an instrumental resolution of 6–9meV by Joe Ho *et al.*[3] But it is often difficult to determine molecular structures experimentally. The accuracy of these calculations is of necessity limited when the number of electrons in transition-metal clusters is very large. There are three basic theoretical approaches available for application to small clusters: (1) the semiempirical methods, e.g., Huckel, complete neglect of differential overlap, and tight-binding linear combination of atomic orbitals schemes; [4] (2) the one-electron self-consistent field methods, e.g., Hartree–Fock and local-density models;[5] (3) the many-body methods, e.g., generalized-valence-bond and configuration-interaction methods. These calculations have indicated that the ground state geometries of small Cu_n and Na_n clusters are similar to some extent.[6,7] Moreover, an accurate determination of the equilibrium geometries of the clusters is an essential prerequisite to interpret the photoelectron spectra measured recently.[5] The sensitivity of the electronic structure to the geometry is an interesting property that can be utilized in a combination of experiment and theory. For example, if two different geometrical structures are obtained and their electron affinities or the gaps of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are

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quite different, a comparison with the experimental values will decide which of the two geometrical structures is the actual ground state.

In this paper, the geometrical structure and energy level distribution of small $Cu_n(n \leq 9)$ clusters are investigated with an accurate density functional method (DFT). The relation of cluster properties to cluster size is computed and discussed.

2. Computational detail

Calculations were carried out using the popular density functional: the 'hybrid' Becke 3 term Lee Yang, Parr (B3LYP) functional, which is a three-parameter mixture of density functional and 'exact' Hartree–Fock exchange.[8] DFT is nowadays one of the best methods to study small and medium size systems, it yields results comparable to those obtained with standard correlated *ab initio* methods; however, the computational cost is similar to the lowest level of Hartree–Fock without the important electron correlation contribution. The effective core potential (ECP) and basis set with a double-ξ type suggested by Los Alamos National Laboratory (LANL2DZ) have been used to optimize the geometry of all topologically different clusters. For Cu the core electrons were defined as $[core]5s^25p^65d^{10}6s^1$. In order to have only one electron with the same angular momentum quantum number l, the positive ion with the electron removed from the outer $(n+1)$ orbital was used as the starting point for generating the ECPs. Then, the 19 valence electronic pseudo-orbitals were defined with the ns, np, and nd orbitals. The numerical potentials were derived and fitted to analytic Gaussian functions in the form $r^2[U_l - U_L], l = 0, 1, \ldots, L-1, r^2[U_L - N_c/r], l = L$, where L is the lowest angular momentum not represented in the core and N_c is the number of core electrons. The Gaussian functions have the form $\sum_k d_k r^{n_k} \exp[-\xi_k r^2]$, where n_k =0,1, or 2. The analytic representations for the ECPs are given in Ref.[9].

Since there are controversies over the geometrical shape of transition-metal clusters containing a few atoms, the total energy has been calculated and the geometrical structure with the lowest energy was chosen as the ground state geometry. All calculations were performed using the Gaussian 98 program. When the atomic number of the cluster is less than 6, the default self-consistent field convergence of 10^{-8} was used. And for the larger clusters ($n \geq 6$), the computation could not converge except to a 10^{-5} tolerance. The ground states of pure Cu clusters have the lowest possible multiplicity that can be obtained for a given number of unpaired electrons.

3. Results and discussion

3.1. Equilibrium geometry

The ground-state structures of copper clusters up to the nonamer were optimized by the B3LYP method with ECP, and the equilibrium geometries of these minima are illustrated in Fig.1. For the Cu_2 dimer, the geometry optimization led to a predicted equilibrium bond length of 0.22592nm for the $X^1\Sigma_g^+$ ground state with a binding energy of 1.0082eV and vibrational frequency ω_e=256.1462cm^{-1}, which are in excellent agreement with experiment. The ground state of Cu_3 is found to be an X^2B_2 state corresponding to a Jahn–Teller distortion of an equilateral triangle geometry (R=0.2357nm, θ=74.1732) which is found to lie 0.08241eV below the linear structure ($D_{\infty h}$), in good agreement with the ESR spectrum studies.[10] Since there is a controversy about the geometrical shape of transition-metal clusters containing a few atoms, the binding length and binding energy of copper clusters in linear $D_{\infty h}$, planar C_{2v}, and three-dimensional T_d or O_h symmetry have been calculated. It is shown that the rhombus capping an edge of the trimmer is the most stable structure of the copper tetramer, in analogy with other metals having one valance electron.[11] The most stable pentamer and hexamer are planar trapezoidal and planar triangle where the extra atom caps an edge of the rhombus, or caps an edge of trapezoidal respectively. For the septimer, the geometries become three-dimensional instead of a planar. Thus, Cu_7 has pentagonal bipyramidal structure, while Cu_8, Cu_9 has one or two atom caps on the pentagonal bipyramidal structure.

The average distance between atoms in the cluster can be defined as $\bar{R} = \frac{1}{N_b}\sum_i R_{ij}$, where R_{ij} is the nearest-neighbour distance less than 15% of the minima distance. The average coordination number is the average number of nearest neighbours within a given cut-off distance (0.2875nm), CN=$\frac{1}{n}\sum_i in_i$, i being the index of the nearest-neighbour atoms. The geometrical parameters of copper clusters containing up to nine atoms are summarized in Table 1.

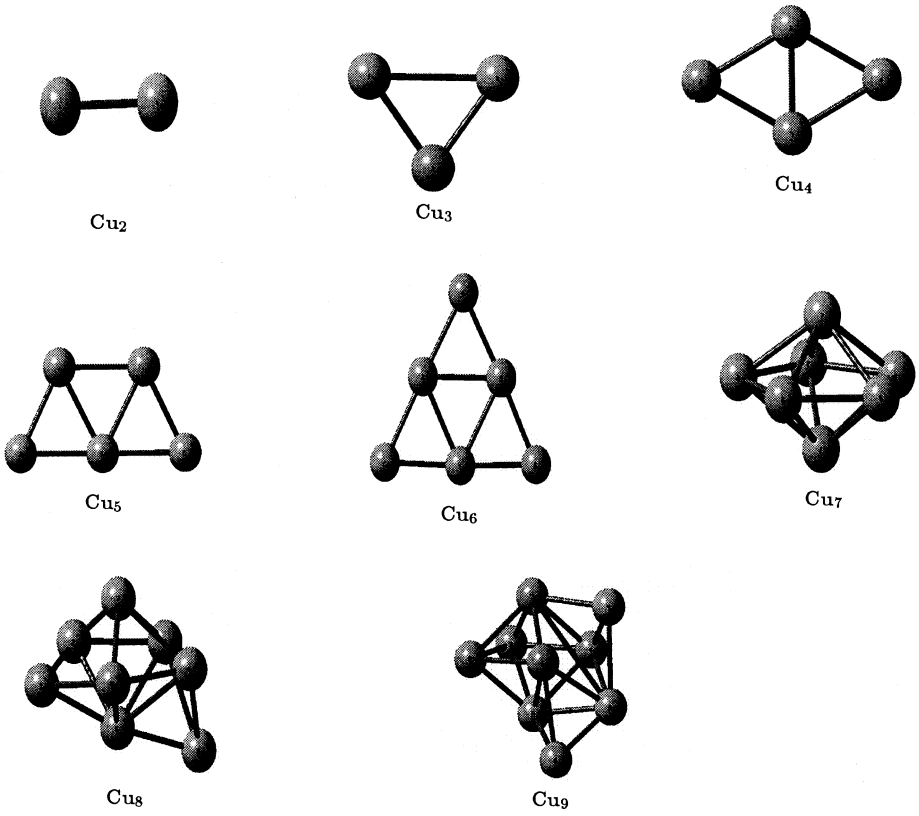


Fig.1. Ground-state structures of small copper clusters (Cu_{2-9}).

Table 1. The geometry parameters of Cu_n ($n \leq 9$).

cluster	symmetry	E/arb. units	$\bar{R}$/nm	CN	AE[a]/eV	Expt./eV[12]
Cu_2	$D_{\infty h}$	−392.3077	0.22592	1	2.0164(1.0082)	2.078
Cu_3	C_{2v}	−588.4612	0.24854	2	3.0162(1.0054)	3.05
Cu_4	D_{2h}	−784.6592	0.24232	2.5	5.2248(1.3062)	
Cu_5	D_{2h}	−980.8434	0.24337	2.8	7.0605(1.4121)	
Cu_6	C_{2v}	−1177.0518	0.24466	2.7	9.5532(1.5922)	
Cu_7	D_{5h}	−1373.2358	0.25080	4.28	11.3820(1.6260)	
Cu_8	C_s	−1569.4352	0.25156	4.5	13.6304(1.7038)	
Cu_9	C_s	−1765.6084	0.25793	4.67	15.1668(1.6852)	

a: The values in parentheses are the atomization energies (AEs) per atom.

From Table 1, we can see that the atomization energies (AEs) of copper clusters increase rapidly with cluster size. For example, Cu_4 is 1.3062eV more stable than the Cu_2 molecules, while the AE per atom for the Cu_9 is less than Cu_8's. Since the Cu_8 cluster corresponds to an especially stable closed shell structure, the decreased per atom atomization energy of the Cu_9 compared with Cu_8 is expected. However, despite this large increase, the AE per atom for the Cu_9 is less than half that of the bulk Cu (3.50±0.01eV)[13] due to the much smaller coordination number. The coordination number increases monotonically with size, and converges to 12, the value of the bulk.

3.2. Energy level distribution and electronic properties

For the Cu atom, the d shell is filled with 10 electrons, and the valence shell contains a single s electron. In the bulk, the d band is buried below the Fermi level. Thus, in the copper clusters, these valence electrons are too free-electron-like to show the shell structure. Meanwhile, since the electrons are limited by the border, the energy spectra will become split and not continuous when the size of the metal reduces to nano-level. With fixed geometries of small copper clusters (Fig.1), the B3LYP method has been used to inves-

tigate the energy levels of the valence electrons and the d-electrons. HOMO–LUMO gap (HLG), electron affinities (EAs) and ionization potentials (IPs) for the Cu_n ($n \leq 9$) clusters have been studied and are listed in Table 2, where the structures of the copper cluster negative and positive ions have been optimized with the same method and the same valence basis set. The optimized structures of the negative and positive ions are very similar to those of the neutrals except for the trimer where the negative ion is linear and the neutral is triangular.

Table 2. HOMO, LUMO, HOMO–LUMO gap (HLG), electron affinities (EA) and ionization potentials (IP) for the $Cu_n (n \leq 9)$ clusters.

cluster	HOMO/arb. units	LUMO/arb. units	Fermi level/eV	HLG/eV	EA/eV	IP/eV
Cu_2	–0.20543	–0.08581	–3.9626	3.2551	0.6732	7.9301
Cu_3	–0.14894	–0.09771	–3.3559	1.3941	1.9114	5.7417
Cu_4	–0.17470	–0.10467	–3.8011	1.9057	1.3353	6.5886
Cu_5	–0.16732	–0.07970	–3.3610	2.3843	1.7486	5.9861
Cu_6	–0.20207	–0.08280	–3.8759	3.2456	1.0093	7.1954
Cu_7	–0.16291	–0.07884	–3.3750	2.2799	1.8281	5.8854
Cu_8	–0.17631	–0.09345	–3.6704	2.2548	1.3089	6.1902
Cu_9	–0.14169	–0.09369	–3.2026	1.3062	2.1957	

Table 2 provides information about the Fermi levels and the energy gaps between the HOMO and the LUMO for the Cu_n ($n \leq 9$) cluster. The Fermi levels, defined as the highest occupied orbital energy, have the remarkable even–odd effect. This is due to the fact that a cluster with a doubly occupied HOMO level is more stable and has a higher Fermi level than clusters with a singly occupied HOMO. However, the HLGs have not the even–odd effect and the HLG of the Cu_2 and Cu_6 are almost the same and the largest.

EAs and IPs as functions of cluster size are shown in Fig.2. For Cu_2–Cu_5, the calculated results are in excellent agreement with experiment. The major feature in the dependence of EAs on cluster size is the strong alternation between even and odd numbered cluster. Meanwhile, the IPs have the opposite alternation patterns (even>odd). The alternation in EAs and IPs are essentially an electron pairing effect, resulting from the circumstance that each atom in the cluster contributes a single valence electron to the bonding orbitals. Even anion clusters have an odd total (n+1) of valence electrons and the HOMO is singly occupied (Cu_2^-, Cu_4^-, Cu_6^-, Cu_8^-); odd anion clusters have an even number of electrons with two electrons in the HOMO. The electron in a doubly occupied HOMO will feel a stronger effective core potential because the electron screening is less effective for electrons in the same orbital than for inner shell electrons. Thus the binding energy of a valence electron within an odd anion cluster is larger than that of an even one. In contrast, the ionization potentials of the odd clusters, which have an open-shell electron, are less than the clusters that have a closed shell.

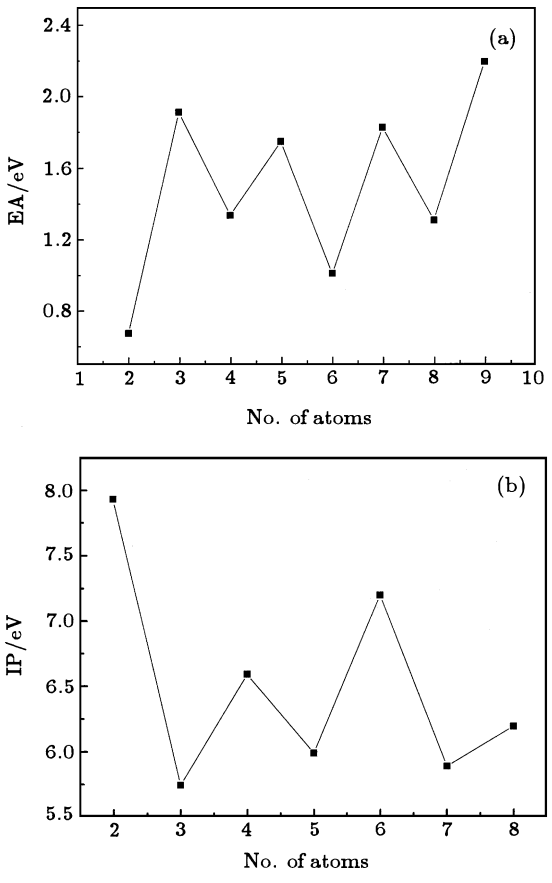


Fig.2. The curve of EAs and IPs vs the cluster size.

4. Conclusions

The calculation performed here are the most accurate and systematic to date for the copper clusters $Cu_n (n \leq 9)$. As the group IA and IB metals have different crystal structures, different cluster geometry will appear for clusters larger than the pentamer clusters. The most stable structures of copper clusters are found to be different from that of the sodium cluster: Cu_n become three-dimensional at 7 atoms but not at 6 atoms.

The most remarkable characteristic of the copper clusters, such as HLG, EA and IP, show a non-monotonic change as functions of cluster size with the presence of the even–odd effect. This is due to the almost complete lifting of the orbital degeneracy; clusters with a doubly occupied HOMO level are more stable and have a larger electron affinity and ionization potential than clusters with a singly occupied HOMO.

Photoelectron spectroscopy studies of cluster anions can give direct information on the structure of electronic energy levels, because the sensitivity of the electronic structure to the geometry is an interesting property that can be utilized in a combination of experiment and theory. For example, if two different geometrical structures are obtained and the EAs, the IPs or the HOMO–LUMO gaps are quite different, a comparison with the experimental values will decide which of the two geometrical structures the actual ground state is. This procedure is much more reliable than making a decision based only on the calculated total energies. Therefore, the calculation method in this study can provide some important chemical information on the copper clusters.

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